

1. INTRODUCTION

The purpose of this report is to document the results of laboratory studies on the mobilities of selected radionuclides in sedimentary interbed from the Subsurface Disposal Area (SDA) at the Idaho National Engineering and Environmental Laboratory (INEEL). The work was conducted in support of risk analyses for the Waste Area Group 7 (WAG 7) Comprehensive Remedial Investigation and Feasibility Study. The principal exposure pathway of concern for WAG 7 involves the Snake River Plain aquifer, which lies approximately 200 m below the SDA. In the risk analyses, contaminant transport from the waste trenches to the aquifer is based on classical advection/dispersion/sorption theory in which the interaction between the contaminant and the solid phase is conceptualized as a linear, reversible, sorption process. In this approach, contaminant mobility is inferred from distribution coefficients measured in batch partitioning experiments. Plutonium and americium mobilities estimated through this approach are extremely low, and interbed is predicted to be an effective barrier to migration. However, field measurements below the SDA suggest that americium and plutonium may have penetrated one or more interbed layers.

There are a number of observations, from both field and laboratory investigations, suggesting that some contaminants of concern at Department of Energy sites can travel faster than predictions based on classical advection/dispersion/sorption models of the type used for the Interim Risk Assessment at WAG 7. There are both hydrological and chemical/geochemical mechanisms, acting either separately or in combination, that can be invoked to explain these observations. The work reported here focused on chemical/geochemical mechanisms that may affect the mobilities of various actinides, especially plutonium, in sedimentary interbed. The initial objective was to determine if high mobility forms of plutonium were possible in laboratory columns eluted with a perched water simulant. As the project progressed, the scope expanded to include uranium and americium, which are important contaminants at the SDA, as well as thorium and neptunium, which are potential analogs for plutonium(IV) and plutonium(V), respectively. The objectives were also extended to include mechanistic explanations for the observed behaviors, which are critical for determining if the phenomena observed in the laboratory setting are relevant to the field. The resulting body of data, in aggregate and in combi-

nation with thermodynamic calculations, not only yields explanations for the transport behaviors observed in the laboratory system, but also provides a basis for identifying the chemical/geochemical processes that are likely to be important under a given set of field conditions. Also included in this report are results of tests performed to examine a limited number of potential experimental artifacts that might limit or prohibit extrapolation of the laboratory findings to the field.

2. BACKGROUND

Overview

The SDA is part of the Radioactive Waste Management Complex at INEEL. It contains shallow pits, soil vaults, and trenches where a variety of low-level, mixed, and transuranic wastes are buried. The Snake River Plain aquifer is separated from the SDA by a thick (approximately 180 m) vadose zone consisting of a layered sequence of fractured volcanic rocks (primarily basalt) and sedimentary interbeds. There are at least 11 basalt layers and 10 interbed layers between the SDA and the aquifer (USGS, 1999). The modeling of contaminant transport from the SDA to the aquifer is an extremely difficult problem because of inherent complexities and uncertainties associated with both the hydrology and the geochemistry. Contributing to the hydrological complexity are questions regarding the integrity (*i.e.* the presence of fractures) and uniformity of the interbed layers, the role of past flood events on contaminant migration, and the relative importance of vertical infiltration of water from the surface versus lateral infiltration from adjacent areas. The geochemical complexity is due to the varied composition of leachate from waste trenches, the changes in chemistry that occur due to contact with the subsurface media, and the assortment of liquid and solid phase processes that may influence contaminant mobility. These processes, which include hydrolysis, precipitation, complexation, colloid formation, ion exchange, and oxidation/reduction, are discussed in detail later in this section.

Relevant Laboratory and Field Data

A key question with respect to transport modeling is whether the geochemical interactions can be adequately approximated by the traditional modeling approach, in which contaminant mobility is inferred from batch sorption experiments. An inherent assumption of the traditional approach is that the contaminant exists in a single physical/chemical form. There is a growing body of evidence suggesting that some contaminants, especially some of the actinides, can exist in multiple physical/chemical forms, each with different mobilities. Fried *et al.* (1974) observed high mobility forms of americium and plutonium in laboratory experiments with volcanic tuff from Los Alamos. They performed two types of experiments. In the first, plutonium and americium were depos-

ited in a depression on the top of a block of tuff. After several “rain-drought” cycles in which the block was showered with water and allowed to dry, cores were extracted from the block. Each core showed two zones of activity as a function of depth. There was a low mobility zone close to the site of deposition that contained the majority of the plutonium and a high mobility zone some distance away that contained less than 1% of the original activity. Small, high mobility components were also observed in column tests with crushed and washed tuff. From these experiments, it was estimated that 1% of the plutonium had a mobility that was 25,000 times higher than the bulk of the plutonium. Thompson (1989) performed column tests with crushed tuff and groundwater (“J-13”) from the Nevada Test Site. He observed some of the plutonium, americium, and neptunium to travel through the columns at approximately the same speed as tritium. For plutonium, the high mobility fraction depended on the oxidation state. It was as high as 70% for plutonium(V) and/or plutonium(VI), but it was generally less than 10% for plutonium(IV). The behavior of americium was similar to that of plutonium(IV) and the behavior of neptunium was similar to that of plutonium(V)/plutonium(VI). In previous work performed in our laboratory, column experiments were conducted with basalt and sedimentary interbed from INEEL. Cobalt, plutonium and americium were observed to have multiple mobilities, presumably due to multiple physical/chemical forms; but uranium, cesium, and strontium did not (Fjeld *et al.*, 2000).

There is also field evidence suggesting multiple mobilities. Based on an examination of field data at the Savannah River Site (SRS), Looney *et al.* (1987) incorporated high mobility fractions for selected contaminants in risk assessments of waste management activities at the site. The contaminants exhibiting evidence of high mobility transport were barium, cadmium, chromium, lead, mercury, cobalt, strontium, cesium, uranium, and plutonium. Kaplan *et al.* (1994) found varying fractions of fast moving plutonium, uranium, americium, and curium in an acidic groundwater plume at SRS. Penrose *et al.* (1990) found elevated plutonium and americium concentrations in a small aquifer at Los Alamos. Although Penrose *et al.* attributed the presence of the radionuclides to colloidal transport through the aquifer, Marty *et al.* (1997) subsequently made a case for infiltration of surface water. Buddemeier and Hunt (1988) and Kersting *et al.* (1999) observed high mobility transport of radionuclides at the Nevada Test Site. Based on field tracer experiments with lanthanides, McCarthy *et al.* (1998) concluded that high mobility forms of americium at the Oak Ridge National Laboratory were due to association with natural organic matter.

Actinide Chemistry

The actinides are heavy metal cations that can exist in the environment in several different oxidation states, and their behavior in the environment is often dictated by the oxidation state of the ion under the conditions present (Kim, 1986). Some actinides are quite stable with respect to oxidation state. For example, americium and thorium are generally only found in the III and IV oxidation states, respectively. Others may be present in multiple oxidation states. Neptunium can exist as IV and V and uranium as IV and VI. At the extreme is plutonium, which can exist in up to four oxidation states (III, IV, V, and VI) simultaneously (Cleveland, 1970). For the groundwater and perched water typical at INEEL, americium is III, thorium is IV, neptunium is V, uranium is VI, and plutonium is IV and V. Because of the similarities in atomic structure among the actinides, different elements with the same oxidation state are expected to exhibit similar chemical behavior (Silva and Nitsche, 1995). Thus, thorium (IV) should behave as plutonium(IV); neptunium(V) should behave as plutonium(V), and so on.

Due to the complex chemistry that exists under environmental conditions, it is necessary to examine several aspects of actinide chemical behavior. There are five facets of actinide chemistry that can significantly affect the migration of actinides through the subsurface - solubility, complexation, sorption, colloid formation, and redox conditions. Each process is often difficult to single out because of the influence of the others. This section provides a basic overview of these areas of actinide chemistry as they pertain to the five radionuclides studied in these experiments - americium, thorium, neptunium, uranium, and plutonium.

Solubility

Generally, the solubilities of metal ions in natural water systems are regulated by the formation of hydroxide or carbonate precipitates (Stumm and Morgan, 1981). To a lesser extent, solubilities are also affected by the presence of other ligands, such as fluoride, sulfate, silicate, and phosphate (Nitsche and Edelstein, 1985). The mobility of a metal species generally decreases with decreasing solubility because it can become trapped within the soil matrix when it precipitates out of the dissolved phase.

Due to variations in oxidation state and groundwater chemistry and the difficulty in truly reaching equilibrium, universally applicable solubility data for the actinides in natural waters do not exist. The solubility of americium, which is initially present as the Am^{3+} ion, is primarily dependent on the carbonate concentration in solution. Between pH 7

and 9 its solubility is limited by the formation of $\text{AmOHCO}_3(\text{c})$ and can fall below 10^{-8} M; above pH 9, however, further carbonate complexation actually increases its solubility (Hobart, 1990; Langmuir, 1997). These solubility predictions are also strongly influenced by the concentration of the carbonate/bicarbonate ions. At low carbonate concentrations and pH 9, the crystalline AmCO_3OH is predicted to be present.

Plutonium(IV) can hydrolyze in natural waters to form the amorphous polymer $\text{Pu}(\text{OH})_4 \times \text{H}_2\text{O}$, which has a very low solubility product, approximately 10^{-56} (Cleveland, 1970). Upon sufficient aging, this amorphous polymer can attain a crystalline structure, which increases the difficulty of dissolution (Rai and Ryan, 1982). It is also reported that plutonium(IV) solubility tends to be high in solutions in which the concentrations of carbonate and fluoride ions are also high (Nash *et al.*, 1988). Furthermore, α -radiolysis may complicate matters by creating oxidation products that oxidize the Pu^{4+} ion to the more soluble higher oxidation states. For example, it was found that, over an aging period of 1300 days, a sample of ^{238}Pu had remained in the amorphous Pu^{4+} polymer while a sample of the less radioactive ^{239}Pu achieved the crystalline form (Nitsche, 1991). However, since radiolysis generally occurs at much higher plutonium concentrations than those typically encountered in environmental settings, this process is probably not important.

Thorium, which exists primarily in the IV oxidation state in natural waters, behaves similarly to Pu^{4+} , generally having a low solubility which is limited by the formation of the $\text{Th}(\text{OH})_4$ amorphous polymer and subsequent crystalline solid. Thorium may also form complexes with sulfate, fluoride, carbonate and phosphate in natural waters, which may increase its solubility (Lieser and Hill, 1992).

In the V oxidation state, plutonium is present as PuO_2^+ , which is typically quite soluble (Watters, 1983). However, the amounts of all oxidation states of plutonium in solution are limited by the amount of $\text{Pu}(\text{OH})_4$ in solution (Choppin and Stout, 1989). Also, at concentrations above 10^{-8} M, the PuO_2^+ ion may disproportionate or be reduced to form Pu^{4+} , which can further complicate its solubility (Bagnall, 1972; Choppin, 1994b). Plutonium(V) most readily disproportionates in highly acidic conditions; however, at near-neutral pH, it is the most observed oxidation state of plutonium in natural waters (Keller, 1971).

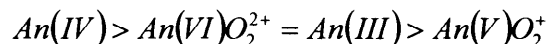
Neptunium, in its V oxidation state, also exists as an oxygenated ion, NpO_2^+ . Neptunium is quite soluble in this form. In one study it was reported that under normal geo-

chemical conditions, aqueous neptunium concentrations may be as high as 10^{-4} mol/L, which is two orders of magnitude higher than the highest soluble concentrations of the other transuranic ions (Kim, 1986). The solubility of neptunium, like that of plutonium, is also affected by the formation of $\text{Np}(\text{OH})_4$ polymer, although neptunium(IV) is much more prone to oxidation to neptunium(V) in near-surface conditions (Morse and Choppin, 1991). It has also been found that the presence of carbonate ions may increase the solubility of neptunium(V) above pH 9 (Nakayama *et al.*, 1988).

Uranium, which is present in the VI oxidation state (as the UO_2^{2+} ion), is also very soluble, as it tends to form carbonate complexes that keep it in solution (Morse and Choppin, 1991). UO_2^{2+} reacts with hydroxide to form $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$ (the mineral Schoepite), which limits the amount of uranium in solution. Since the formation of Schoepite takes on the order of several weeks to reach equilibrium (Silva, 1992), it would not be important in the short term but it could be important in the long term. The solubility of the uranyl ion may also be affected by the presence of silicates in some environments (Choppin *et al.*, 1994a).

Complexation

Complex formation is an important aspect of actinide ion behavior in natural waters. Complexes can alter solubility, solid surface characteristics, and sorption ability, which in turn can greatly affect migration (Snoeyink and Jenkins, 1980; Jensen, 1980). Typically, actinide cations, considered hard acids, preferentially interact with hard bases such as fluoride or oxygen rather than nitrogen, sulfur, phosphorous, or other softer bases (Morse and Choppin, 1991). Furthermore, complexation behavior is mostly a function of oxidation state rather than specific element. Because actinides with the same oxidation state have similar ionic radii, it is possible to make generalizations concerning their complexation behavior. Typically, the relative affinity for actinides to form complexes follows the order:



As a result, actinides in the IV oxidation state tend to form the strongest complexes and the V actinides form the weakest (Hobart, 1990). In addition, the complexation strengths of the various ligands present in the groundwater are also an important factor in determining the complexes that are formed. The relative strengths of some common inorganic groundwater ligands are (Silva and Nitsche, 1995):



Since complex formation is dependent primarily on oxidation state and on the ligands present, it is necessary to examine the behavior of the four oxidation states (III, IV, V, and VI) that are studied in this work.

Americium, in the III oxidation state, tends to form several different carbonate complexes in a natural system. In the pH range of 7.9 to 9.1, the most prevalent soluble americium-carbonate species are $Am(CO_3)_2^{1-}$, $Am(HCO_3)_2^{1+}$, and $Am(OH)(CO_3)_2^{2-}$ (Bidoglio, 1982; Newton and Sullivan, 1985), and they are considered to be the major solution species (Silva, 1984). With the typical amounts of carbonate present in groundwater under natural conditions, americium(III) generally forms carbonate species, despite the presence of other ligands (Nitsche, 1991). It must be noted, however, that there are discrepancies in the literature regarding the complexation of americium and the specific carbonate complexes that are formed (Silva *et al.*, 1995).

As noted in the section on solubility, thorium and plutonium in the IV oxidation state generally form hydroxides under natural conditions. In a carbonate solution, it has been found that thorium(IV) can form $Th(CO_3)_4^{4-}$, $Th(CO_3)_5^{6-}$, and $Th(CO_3)_6^{8-}$ (Hobart, 1990). However, it is believed that at natural pH levels, both organic and inorganic complexes of thorium(IV) are insignificant relative to $Th(OH)_4$ (Lieser and Hill, 1992). There are uncertainties in the literature regarding the carbonate complexation of plutonium(IV) due to its variable oxidation state in natural waters. It is thought that $Pu(CO_3)_2^{2-}$, $Pu(OH)_2(CO_3)_2^{2-}$, and $Pu(OH)_4(CO_3)_2^{4-}$ are the most prevalent plutonium-carbonate species at high carbonate and bicarbonate concentrations; but, as with thorium(IV), the plutonium(IV) hydroxide is still the dominant plutonium species at natural carbonate levels (Yamaguchi *et al.*, 1994; Nitsche and Silva, 1996).

The actinides in the pentavalent oxidation state, plutonium and neptunium, are the least likely to form complexes of the elements under study here. Both PuO_2^{+} and NpO_2^{+} are quite resistant to hydrolysis and carbonate complexation at near neutral pH (Jensen, 1980). In carbonate solutions at high pH, pentavalent neptunium can form both hydrolysis species and mixed hydroxy-carbonate species (Neck *et al.*, 1997). However, since plutonium(V) is much more susceptible to reduction or oxidation than neptunium(V), they cannot be expected to behave similarly under all conditions.

Uranium, which occurs as UO_2^{2+} , is quite likely to form complexes with several different groundwater ligands. It has been found that uranium(VI) complexes with carbonate, forming $\text{UO}_2(\text{CO}_3)$, $\text{UO}_2(\text{CO}_3)_2^{2-}$, and $\text{UO}_2(\text{CO}_3)_3^{4-}$, which play an important role in migration (Brookins, 1989). Uranium also forms complexes with the fluoride ion, forming several species ranging from UF^{3+} to UF_6^{2-} , and also may hydrolyze to form $\text{UO}_2(\text{OH})^+$, $(\text{UO}_2)_2(\text{OH})_2^{2+}$, and subsequent polymers (Kohler *et al.*, 1996). Furthermore, under acidic conditions, uranium may complex with sulfate, producing $\text{UO}_2(\text{SO}_4)_2^{2-}$ (Brookins, 1989).

Sorption

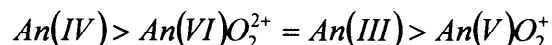
Sorption behavior is an important factor to consider when studying actinide migration. Even temporary sorption of an actinide solute onto a solid surface can significantly retard its transport (Deutsch, 1997). Typically, sorption occurs through an ion exchange process in which negatively charged minerals in clay and soils electrostatically interact with the positively charged actinide cations (Livens *et al.*, 1996). This ion exchange process is often pH dependent, and competition may occur for exchange sites between different cations. Chemisorption may also occur through a chemically driven process, in which a chemical bond is formed between the adsorbent surface and the adsorbing species. This type of sorption is basically irreversible.

Generally, the chemical parameters in a natural system that have the most significant influence on actinide sorption behavior are redox conditions (affecting the oxidation state of the actinide species), pH (affecting the amount of hydrolysis), and the presence of complexing agents (Allard *et al.*, 1982; Dozol and Hagemann, 1993). The ionic strength of the groundwater solution has also been shown to have important effects on the sorption of actinides (Kaplan *et al.*, 1998). Since the lower valence actinides (americium, plutonium, and thorium) are more likely to undergo hydrolysis and hydroxy-carbonate complexation, they are also more likely to be involved in some sorption process at the soil surface. The actinides at the higher oxidation states (plutonium, neptunium, and uranium) are typically not sorbed to a large extent. However, because of chemical reduction and complexation, the higher valence actinides may be sorbed more than expected (Jensen, 1980; Choppin and Stout, 1989; McCubbin and Leonard, 1995).

Colloid Formation

The formation of colloids can play an important role in actinide migration. Both organic and inorganic colloids are ubiquitous in natural systems. Actinide colloids may be formed by polynucleation followed by agglomeration ("real" or "true" colloids), or by associating through sorption or ion exchange onto existing groundwater colloids ("associated colloids"). It is believed that natural organic colloids have the largest impact in colloidal transport, though inorganic colloids may have a significant influence as well (van Gunten and Benes, 1995).

As with sorption, the formation of actinide colloids is complex and highly dependent upon solubility, hydrolysis, complexation, and, ultimately, oxidation state of the actinide in question. The relative tendency to generate real colloids among the different actinide oxidation states is the same as the tendency for complexation and hydrolysis that was indicated above (Kim, 1991):



This suggests that plutonium and thorium, in the IV oxidation state, most readily undergo real colloid formation. The An(IV) hydroxide agglomerates into an oxy-hydroxide colloid form, which can have a high mobility if it remains suspended or a low mobility if it becomes trapped in the soil matrix. The complexation ability of An(VI) is well documented, but the colloid formation ability has not been widely investigated. The trivalent actinides also undergo hydrolysis and thus form real colloids, but those colloids are less stable than their tetravalent counterparts and are more prone to sorption onto solid surfaces. The actinides in the V oxidation state are not thought to undergo significant colloid formation (Ramsay, 1988; Nagasaki *et al.*, 1998).

The generation of associated colloids is of concern because of their potential for increased transport. Depending on the electrostatic charge of the colloid relative to the surrounding media, actinide associated colloids have the ability to move faster than the groundwater (Nagasaki *et al.* 1997). Typically, the formation of associated colloids is a function of the sorption ability of the actinide species present, which can be affected by pH, groundwater chemistry, redox potential, *etc.* For actinides in all oxidation states, associated colloid formation may be abated in the presence of a strong complexing agent, such as carbonate or an organic ligand like EDTA or humic acid (Kim, 1991).

Redox

Actinide speciation and mobility is influenced by the redox potential of the ground-water and surface-active constituents such as reduced iron and manganese of sediments (interbed soils) in contact with the groundwater. Most E_H -pH phase diagrams presented in the literature address the $An-C-O-H$ and $An-O-H$ systems. In many natural subsurface environments, pH values range from near neutrality to >9 , and E_H values may vary between -0.1 and $+0.6$ volts. Phase diagrams generally reflect these ranges and may be found for the actinides studied in this investigation. Presented in this basic review are E_H -pH diagrams for the $An-C-O-H$ system. A collection of the diagrams is presented in E_H -pH Diagrams for Geochemistry (Brookins, 1987). Excerpts from the text for americium, thorium, plutonium, neptunium and uranium are noted in the following discussion to suggest likely predominant actinide species present in groundwaters at the SDA. The perched water simulants used in this investigation were formulated from Wood and Low (1986) and contain oversaturation concentrations of several anions and cations resulting in solid phases not considered in Brookins' review. The presence of these solid phases may influence the mobility of the actinides and therefore will be discussed later in this report.

A collection of the more pertinent phase diagrams used in this investigation is included in Appendix A. These phase diagrams are presented for the $An-C-O-H$ system and generally allow the reader to review likely solid and aqueous species in the E_H -pH range for most natural systems. Thermodynamic data used to calculate these phase regions for important actinide species are also listed in Brookins (1987).

It is interesting to note that at pH 8, within an E_H range of 0.1 to 0.4 and in the presence of carbonate, solid species for each of the actinides included in this investigation are predicted. Thermodynamic data for americium predicts $Am_2(CO_3)_3$; for plutonium, PuO_2 ; for neptunium, NpO_2 ; and for thorium, ThO_2 . However, soluble uranyl carbonate species are predicted for uranium(VI). It is generally accepted that the cation $An(IV)$ is hydrolyzed to $An(OH)_4$, which ages to AnO_2 in most natural settings.

3. MATERIALS AND METHODS

Water Simulants

Several distinctly different chemical compositions of perched water were used for column and batch experiments as water simulants. All perched water simulants were formulated from data provided by Wood and Lowe (1986) for the Snake River Plain Aquifer. The mean, maximum, and minimum concentrations of the major cations and anions are given in Table 3.1. Compositions of the various perched water simulants used in this investigation are also listed in the table. These simulants include (1) a perched water simulant (PWS), which is formulated from all of the major cations and anions found in the Snake River Plain Aquifer and includes humic acid (HA) and ethylenediaminetetraacetic acid (EDTA); (2) a modified perched water simulant (MPWS), which is identical to the PWS but does not contain HA and EDTA; and (3) several MPWS formulations in which specific chemical constituents were removed, *e.g.* MPWS-F⁻ denotes a modified perched water simulant minus the fluoride ion. Each of the simulants was prepared using reagent grade chemicals and distilled water. Dilute hydrochloric acid and sodium hydroxide were used to adjust pH.

Sedimentary Interbed

Sedimentary interbed was collected from the M6S and M7S boreholes at different depths and composited. Interbed samples were collected from depths of 166-177, 322-338 and 386 feet from the M6S borehole and at 213-214 and 329-330 feet from the M7S borehole. Particle size distribution for the composited interbed sample is given in Table 3.2. A more detailed description of the particle size distribution for the interbed samples used to obtain the composited sample is presented in Appendix B. The composited sample was classified as a sandy loam with 17% of the total being composed of particles greater than 2 mm. Of the fraction less than 2 mm, 74% was between 0.05 and 2 mm, 22% was between 0.002 and 0.05 mm and 4% was less than 0.002 mm. Sixty-one percent of the particles less than 2 mm was smaller than 0.25 mm. The composited interbed soil was dry sieved using U. S. Standard Testing Sieves meeting ASTM E-11 specifications and the fraction less than 0.25 mm was retained. Based on USDA classification of soil texture, the <0.25-mm fraction included clays, silts, very fine sand, and fine sand. Most column and batch experiments were conducted using the <0.25-mm fraction.

Table 3.1. Composition of SRPA Groundwater and the Perched Water Simulants Used in this Study

Component	SRPA Groundwater			Perched Water Simulants						
	Mean	Max.	Min.	PWS	MPWS	MPWS (F ⁻)	MPWS (SO ₄ ²⁻)	MPWS (CO ₃ ²⁻)	MPWS (F ⁻ & CO ₃ ²⁻)	MPWS (SO ₄ ²⁻ & CO ₃ ²⁻)
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Ca ²⁺	51	120	5	10.5	10.5	10.5	10.5	10.5	10.5	10.4
K ¹⁺	4	12	0	10	10	10	10	0	0	0
Mg ²⁺	18	54	0.2	17.5	17.5	17.5	2.3	17.5	17.5	2.3
Na ¹⁺	26	140	3.9	570	570	566	450	316	291	174
Cl ¹⁻	28	230	1.8	220	220	218	218	218	217	217
SO ₄ ⁻²	41	218	2.7	350	350	356	NP	355	355	NP
HO ₃ ⁻	220	510	52	750	750	747	749	Trace	Trace	Trace
F ⁻	0.6	11	0.03	20	20	NP	20	20	NP	20
Si ²⁺	50	138	5.8	10	10	10	10	10	10	10
HA	NA	NA	NA	1.3	NP	NP	NP	NP	NP	NP
EDTA	NA	NA	NA	1.3	NP	NP	NP	NP	NP	NP
pH	7.8	9.1	7.0	8.2 ± 0.2	8.2 ± 0.2	8.2 ± 0.2	8.2 ± 0.2	8.2 ± 0.2	8.2 ± 0.2	8.2 ± 0.2
I	0.008	0.02	0.002	0.034	0.034	0.031	0.02	0.02	0.0085	0.019

Table 3.2. Particle Size Distribution for the M6S and M7S Borehole Samples

Sample and Texture		mm	Interbed Composite Sandy Loam
Large		>2	16.7
Small	% Sand	1.00-2.00	12.2
		0.50-1.00	12.2
		0.25-0.50	15.5
		0.10-0.25	20.9
		0.05-0.10	12.9
	% Total		73.7
% Silt		0.002-0.050	22.4
% Clay		<0.002	3.9
% Total Small			100.0

A summary of the major physical and chemical characteristics of the <0.25 mm size fraction of the interbed composite sample is presented in Table 3.3. The exchangeable iron expressed as %Fe₂O₃ and manganese as ppm Mn are presented in addition to the cation exchange capacity data. The dominant minerals represent approximately 90% of the clay minerals present. Extractable iron and manganese data for the samples that were used to obtain the interbed composite sample are presented in Appendix B. A more detailed chemical analysis of the M6S and M7S borehole samples and the composite sample is also presented in Appendix B.

Radionuclide Preparations

Of primary concern to the INEEL was the mobility of plutonium, uranium, and americium through the sedimentary interbed in the vadose zone beneath the SDA. Under natural environmental conditions plutonium can exist in several oxidation states and its mobility is a function of the oxidation state and the species present. Experiments were conducted for americium, uranium, plutonium(IV) and (V) and the plutonium analogs, thorium(IV) and neptunium(V). Column spiking solutions were therefore prepared for each of the radionuclides in the various water simulants noted in Table 3.1. In addition, solutions of tritium and strontium were prepared and studied for quality control purposes.

Spiking solutions were typically prepared by adding a known activity of a radionuclide to the appropriate water simulant followed by a pH adjustment to 8.0 ± 0.2 using dilute HCl or NaOH. The target radionuclide concentration in a spiking solution was typically on the order of 300 Bq/mL. The activity and molar concentrations of americium, thorium, plutonium, neptunium, and uranium in each experiment are given in Appendix C.

Mobility Studies

Apparatus

A block diagram of the flow through column apparatus used in this study is given in Figure 3.1. The apparatus consisted of a peristaltic pump (Masterflex, Cole-Palmer Instrument Co.), column, and fraction collector (Universal Fraction Collector, Eldex Laboratories, Inc.). The columns were fabricated from Plexiglas® tubing 2.1 cm OD, 1.5 cm ID and approximately 8 cm in length. End caps were fabricated from Plexiglas® plate approximately 2.2 cm thick and cut into squares of approximately 4 cm. The center

Table 3.3. Summary of Chemical and Physical Properties of Composite Interbed Used in Batch and Column Studies

Parameter	Composite Interbed
Particle Size Used (mm)	<0.25
Dithionite-Citrate Buffer (DCB) Extractable Fe_2O_3 (%)	1.77
NH_4Oac Extractable Mn (ppm)	1.90
Total Cation Exchange Capacity (meq/100g)	17.39
Dominant Minerals	Montmorillonite, Muscovite and Biotite, Vermiculite

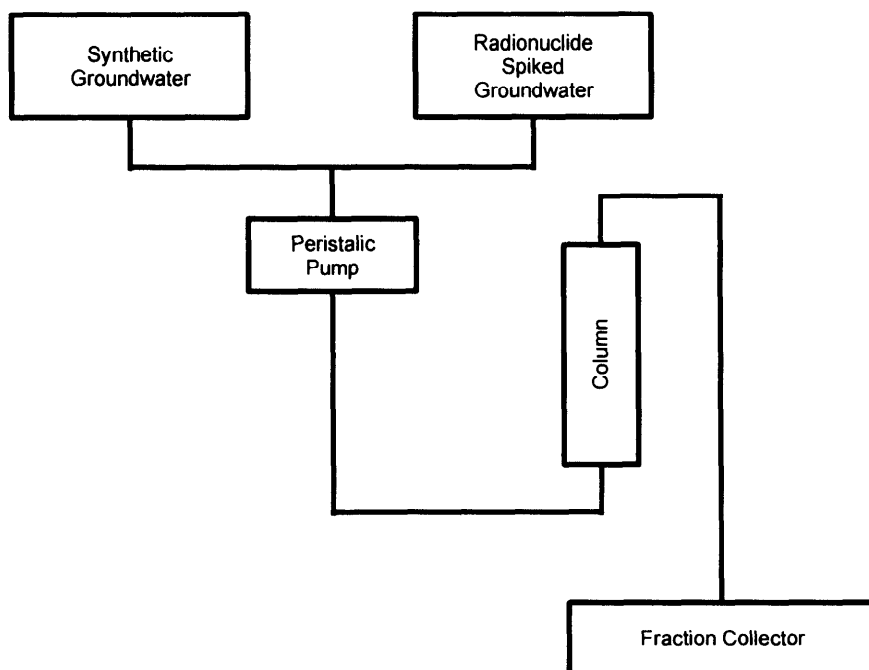


Figure 3.1. Experimental apparatus for column tests

of each end cap was drilled and tapped for 1/16 in. NPT tube fitting grooved to a depth of 0.5 cm to accept an O-ring and the column end. End caps were drilled on each corner to accept 3/16 in. allthread and the columns were clamped together using 3/16 in. wing nuts. The apparatus was interconnected with Masterflex® tubing (size 13) to allow a radionuclide spike (size 13) to allow a radionuclide spike to be introduced into the column and to allow the introduction of a water simulant to elute the radionuclide spike.

Procedures

Typical Studies

Interbed soil columns were dry-packed using the 0.25 mm fraction of the interbed composite. Each column was packed by adding approximately 1 cm of the soil to the assembled column apparatus and lightly tapping the column on a benchtop to compress the soil until the column was completely filled. Before each successive addition of soil to the column, the packed soil surface was agitated using a wooden dowel to avoid creating distinct layers of packed soil. When packed, each column had approximately 30 grams of soil corresponding to a dry bulk density of 1.7 to 1.9 g/mL and a pore volume of about 6 mL.

Column experiments were conducted using both unwashed and washed columns. In most of the experiments, the columns were unwashed, i.e. the first pore volume introduced into the dry column contained radioactivity. The rationale for this approach was that some vadose zone contamination scenarios involve contaminated water contacting dry soil and possibly mobilizing small particles as associated colloids. Washed columns were eluted for approximately 10 pore volumes with the water simulant before spiking with the radionuclide solution. After washing, a nominal one-pore volume spike of the appropriate radionuclide spiking solution was introduced into the column at a flow rate of 0.30 to 0.32 mL/min. Unwashed and washed columns were both eluted with the appropriate water simulant and effluent fractions were collected for ten to several thousand displaced pore volumes.

Redox Studies

Column experiments were also conducted to examine the effect of E_H on the mobility of An(IV) and (V). For the typical column studies outlined above E_H ranged between 50 and 100 mV. Attempts were made to raise the E_H to 400 to 500 mV by ozonating the water simulant for a period of six hours. During this period of time, the oxidized water

simulant was passed through the column in an attempt to oxidize surface functional groups on the interbed soil. The E_H of the water simulant was monitored at both the column influent and effluent. No attempt was made to measure the change in oxidation potential of the interbed soil before and after ozonolysis.

Colloid Studies

Batch and column filtration experiments were conducted to study the formation of true colloids and associated colloids and the attenuation of both types of colloids by the packed interbed columns. For each of these experiments, batch solutions and column eluants were filtered using either syringe filters (Anotop™ 25) to determine particulate fractions from 20 nm to 450 nm (20, 100, 200 and 450 nm) or centrifugal filters (Pall Filtron, Microsep™) to determine particulate fractions below 20 nm nominal (3 and 12 nm). The term 'nominal' refers to the manufacturer specification for ninety percent collection efficiency.

Formation of True Colloids: Experiments were conducted to determine if plutonium oxy-hydroxide colloids would form in a perched water simulant containing both EDTA and humic acid and to evaluate the effect of carbonate on the formation of these colloids. Quadruplicate samples for two sets of the perched water simulant were prepared containing a known activity of plutonium(IV). Samples were analyzed and filtered using an Anotop™ 25 (20 nm) syringe filter approximately one hour after preparation. The filtered sample was then allowed to stand for a period of seven days and filtered again. The seven day filtered samples were allowed to stand for seven additional days and were filtered and analyzed. Additional sets of two tubes were prepared in (1) MPWS without carbonate; (2) MPWS; (3) PWS without EDTA; and (4) PWS without humic acid. These replicate samples were also filtered and analyzed as noted above.

Attenuation of Colloids: To obtain an estimate of the degree to which a packed interbed column attenuates colloids, (both true colloids and associated colloids), a pair of columns were packed with interbed soil sieved to isolate the 106 to 250 μm size fraction. A freshly prepared PWS spiking solution containing plutonium(IV) was introduced onto the column and eluted for 200 DPV. These two columns were not washed prior to the spike and therefore likely contained colloids from the soil matrix. After 200 pore volumes of PWS was passed through the columns, an aged spiking solution that contained ap-

proximately 50% plutonium(IV) true colloids was introduced onto the columns and eluted for 200 DPV. This experiment represented a pair of washed columns. Finally, a suspension of soil colloids was prepared by suspending a mass of the $<106\ \mu\text{m}$ size fraction of the interbed soil in the PWS and filtering with syringe filters to isolate colloids $<200\ \text{nm}$. Plutonium(IV) was added to the colloidal suspension and allowed to equilibrate for a period of 24 hours. These 'tagged' colloids were analyzed to determine the particulate fraction and spiked onto a pair of washed columns and eluted for 200 DPV. Recovery of plutonium(IV) and the fraction of particulate plutonium(IV) was determined. Details of these experiments are summarized in Appendix D.

Tritium Column Checks

Tritium was used as a conservative tracer to determine if the column packing procedure resulted in channeling or short-circuiting. For column studies that were designed to obtain breakthrough data for washed columns, the tritium tracer study was completed prior to spiking the radionuclide of interest onto the packed column. For studies designed to obtain breakthrough data for unwashed columns, the tracer study was performed after the target radionuclide had eluted from the column and the count rate was near background. In either case, tritium was introduced as a one-pore volume finite step spike onto the column and eluted from the column with five pore volumes of the water simulant.

Radionuclide Analysis

All radionuclide analyses were performed with an alpha/beta discriminating liquid scintillation counter (Model 1415, EG&G Wallac). Typically, a one mL aliquot was mixed with 10 mL of liquid scintillation cocktail (Wallac Hi-Safe II) and counted for ten minutes.

It was necessary to determine or verify aqueous phase oxidation states for some of the tests, especially those involving either plutonium(IV) or plutonium(V). Two methods were used, the HDEHP technique of Neu et al. (1994) and the DBM technique of Chopin et al. (1997). Details of the two techniques are given in Appendix E.

Data Analysis

The raw data from the column experiments consisted of radionuclide concentrations, C_i , in incremental effluent volumes, ΔV_i , collected at integrated volumes V_i . The concentrations were normalized by dividing by the concentration in the spike, C_0 , and the

integrated volume was converted to displaced pore volume (DPV) by dividing by the pore volume, V_p . Breakthrough curves were then plotted as normalized concentration as a function of time in DPV.

The breakthrough curves were characterized quantitatively by the retardation factor and corresponding fractional recovery. Retardation factors were calculated as the first moment of the travel time distribution,

$$R = \frac{\int C(V)V dV}{\int C(V)dV}$$

For unwashed columns, this becomes

$$R = \frac{\sum C_i V_i \Delta V}{\sum C_i \Delta V} - 0.5 \frac{V_s}{V_p} + 1$$

where V_s is volume of the spike. The second term in the expression occurs because the spike is introduced as a finite step and the third term occurs because the spike was the first pore volume introduced in the unwashed columns. For washed columns, the third term is deleted. Fractional recovery, f , was calculated from

$$f = \frac{\int_{V_1}^{V_2} C(V) dV}{C_0 \cdot V_s}$$

where V_1 and V_2 are the lower and upper bounds, respectively, of the portion of the breakthrough curve for which the recovery is calculated.

An estimate of the detection limit is shown on many of the breakthrough curves. This estimate is based on Currie's (Currie, 1968) equation,

$$LLD = 2.71 + 4.65\sqrt{B}$$

where LLD is the detection limit (net counts above background) and B is the number of background counts. Since this equation is strictly applicable to a single measurement, it is likely an overestimate when applied to breakthrough curves where trends are observed through a series of consecutive measurements.

4. COLUMN TEST VERIFICATION STUDIES

Tritium

Tritium tests were performed for five selected sets of column experiments to check for channeling. A total of 19 columns were tested. The breakthrough curves for 14 of these were normal in that the leading edge appeared at approximately one DPV, the trailing edge occurred at approximately two DPV, and the curves were symmetric. Presented in Figure 4.1 is one normal curve from each of the five selected sets of column experiments. The breakthrough curves for five of the columns were abnormal. For four of these, the leading edge appeared before one DPV and the curves were skewed to the right. These four curves are presented in Figure 4.2. The early appearance of the leading edge suggests channeling of water through a preferred flow path. Presented in Table 4.1 are fractional recoveries and retardation factors for the 19 tritium tests. It is interesting that the abnormal columns cannot be detected through retardation factor. The mean retardation factor for the normal columns (1.18 ± 0.04) was not significantly different from that for the abnormal columns (1.09 ± 0.16). This is because the early appearance of the breakthrough curve in the abnormal columns was offset by the tailing of the trailing edge. It is also interesting that the retardation factor for normal columns differed significantly from 1.0. The difference, which represents a volume of approximately 1 mL, seems too large to be the result of a systematic experimental bias. (The experimental data were corrected to account for the dead volume (0.5 to 1 mL) in tubing connecting the spike and the columns. No correction was made for the dead space between the tubing connector and the soil; however, this volume is less than 0.2 mL)

Strontium

In many of the actinide column tests, strontium was also included in the spiking solution. Although strontium is present in the SDA and its mobility in interbed is relevant in the site risk assessment, it was included in this study primarily as a form of quality control. The strontium breakthrough curves were used both as a basis for comparison with the actinide breakthrough curves and as a means for monitoring column-to-column variability, both hydraulic and geochemical. Presented in Figure 4.3 are four strontium breakthrough curves from four column

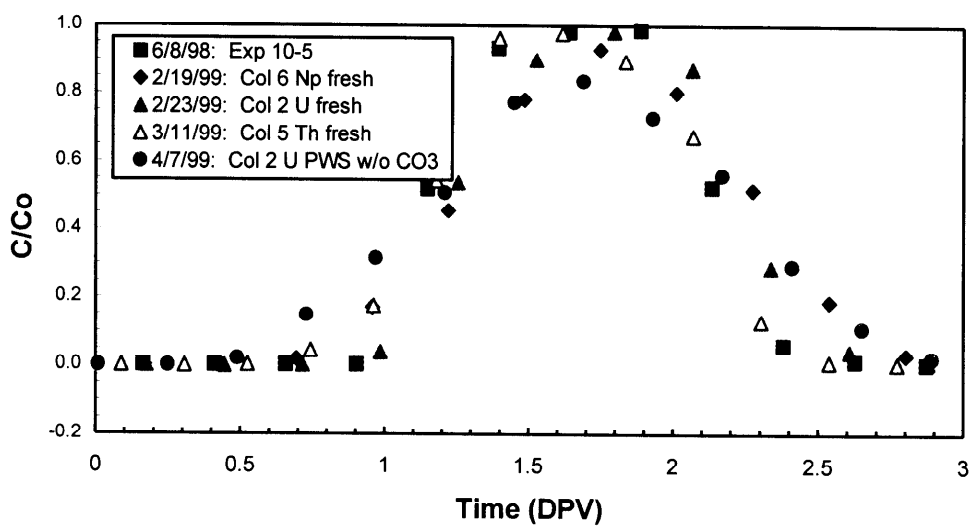


Figure 4.1. Tritium breakthrough curves

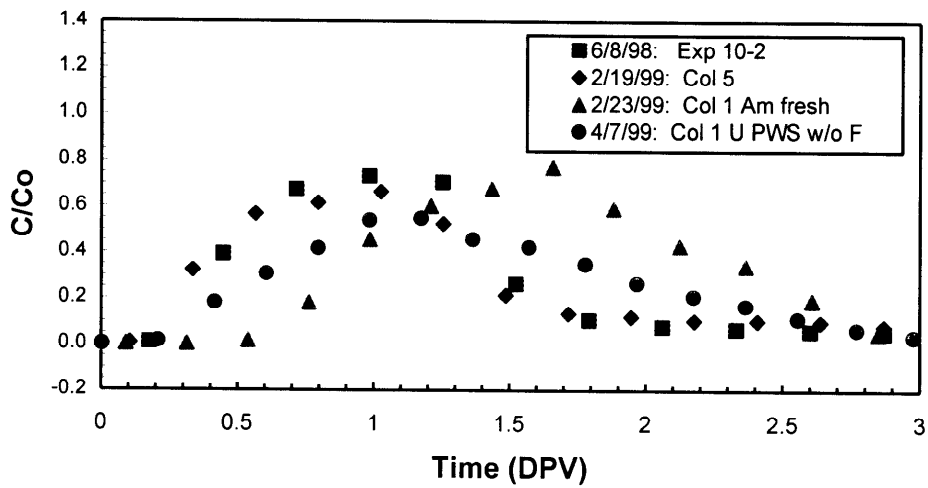


Figure 4.2. Tritium breakthrough curve exhibiting channeling

Table 4.1. Tritium Recoveries and Retardation Factors

Column	Recovery	Retardation Factor	Shape
6/18/98-Exp 10-1	0.79	1.12	Asymmetric peak
6/18/98-Exp 10-2	0.94	0.93	Early breakthrough & skewed right
6/18/98-Exp 10-3	0.99	1.20	OK
6/18/98-Exp 10-5	0.99	1.16	OK
2/19/99-Col 5	0.99	1.28	Early breakthrough & skewed right
2/19/99-Col 6-Np fresh	0.97	1.24	OK
2/19/99-Col 7-Np aged	0.99	1.18	OK
2/23/99-Col 1-Am fresh	0.98	1.16	Early breakthrough & skewed right
2/23/99-Col 2-U fresh	0.99	1.27	OK
2/23/99-Col 3-Am aged	1.01	1.23	OK
2/23/99-Col 4-U aged	0.98	1.21	OK
3/11/99-Col 5-Th fresh	0.96	1.12	OK
3/11/99-Col 6-Pu(IV) fresh	0.98	1.15	OK
3/11/99-Col 7-Th aged	1.00	1.15	OK
3/11/99-Col 8-Pu(IV) aged	0.97	1.18	OK
4/7/99-Col 1-U PWS w/o F	0.96	0.99	Early breakthrough & skewed right
4/7/99-Col 2-U PWS w/o CO ₃	1.01	1.17	OK
4/7/99-Col 3-U PWS w/o SO ₄	0.97	1.12	OK
4/7/99-Col 4-Np/Sr fast	0.98	1.14	OK

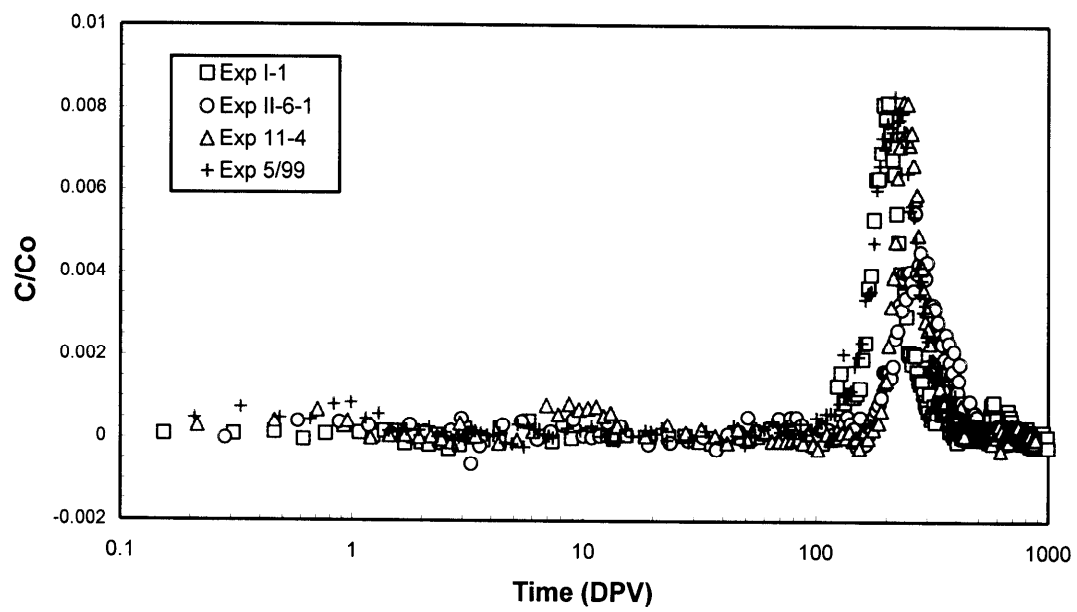


Figure 4.3. Strontium breakthrough curves

tests conducted at different times over the course of the study. Retardation factors and recoveries for these four tests along with those for the other strontium tests are given in Table 4.2. Strontium breakthrough was consistently characterized by a single peak in the 200–300 DPV range. Recoveries were generally within the limits of experimental uncertainty, which is estimated to be 10–15%. Retardation factors for the columns packed with the 106–250 μm size fraction were tightly grouped around 210 and were generally smaller than for the columns packed with the entire fraction smaller than 250 μm . This is likely due to the lower sorptive capacity per unit mass that would be expected for the larger sized particles. The recoveries, which ranged between 83 and 106%, and the retardation factors were not appreciably affected by either EDTA or washing of the column.

The consistency of the strontium behavior, regardless of the simulant, is not surprising from a chemical perspective. It merely reflects the fact that strontium is present as a divalent cation, which is stable with respect to EDTA, HA, carbonate, *etc.*, and that sorption is likely due to adsorption to negatively charged clay minerals. From an experimental quality control perspective, the consistency of the results is reassuring because it suggests some degree of uniformity over the course of the study of the physical/chemical characteristics of the interbed soil samples, the hydraulic properties of the columns, and the experimental procedure in general.

Mean Linear Velocity

Mean linear velocity for the C-D interbed is estimated to be on the order of 2 mm/d or 2×10^{-6} cm/s (Magnuson, 1998). In most of the column experiments, the mean linear velocity was approximately 8×10^{-3} cm/s. This is based on a volumetric flow rate of 0.3 cm³/min, a pore volume of 6 cm³, and a column length of 8.0 cm. Thus, velocities in the column experiments were more than three orders of magnitude higher than the field estimates. This raised an obvious question regarding the effect of mean linear velocity on mobilities determined in column tests. Tests were conducted at both lower and higher velocities. The lowest velocity was 8×10^{-4} cm/s, which corresponds to the minimum flow rate possible with the peristaltic pumps. The results are presented in Figure 4.4, where retardation factor is given as a function of mean linear velocity for strontium, uranium, and neptunium. Although retardation factors increased when the mean linear velocity was reduced from 1×10^{-1} cm/s to 8×10^{-3} cm/s, there was very little change when it was further reduced to 8×10^{-4} cm/s. This flattening of the curve provides some

Table 4.2. Strontium Recoveries and Retardation Factors

Exp	Simulant	Recovery	Retardation Factor	Notes
I-1	PWS	1.05	250	Unwashed column
I-2	PWS	0.92	227	Washed column
I-3	PWS	1.06	280	Unwashed column
I-4	PWS	1.00	230	Washed column
II-6-1	PWS	0.92	294	Unwashed column
II-6-2	PWS	0.92	307	Unwashed column
II-7-1	PWS	0.89	204	Washed column; 106-250 μm
II-7-2	PWS	0.87	215	Washed column; 106-250 μm
II-7-3	PWS	0.89	209	Washed column; 106-250 μm
II-7-5	PWS	0.89	219	Washed column; 106-250 μm
II-11-2	PWS	0.94	315	Unwashed column
II-11-4	MPWS	0.84	289	Washed column
III-F-4	MPWS	0.83	240	Unwashed; 0.1 cm/s

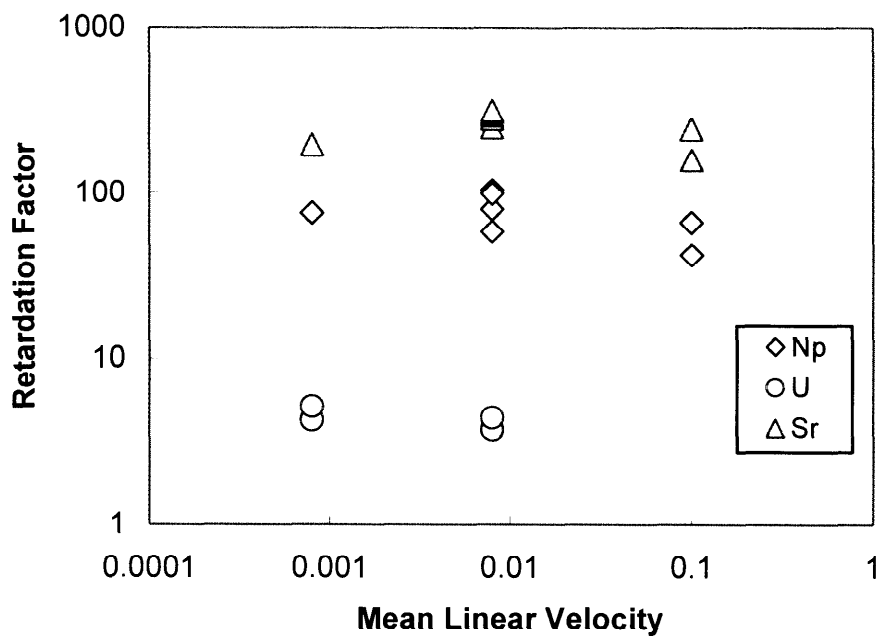


Figure 4.4. Retardation factor as a function of mean linear velocity for strontium, uranium, and neptunium

degree of confidence that mobilities obtained at the typical column test velocity of 8×10^{-3} cm/s are good predictors for lower velocities. However, this extrapolation is not without limitations. While the recoveries for strontium and uranium did not change (essentially 100%), there was a large reduction in recovery (from $\approx 65\%$ to $\approx 20\%$) for neptunium when the mean liner velocity was reduced from 8×10^{-3} to 8×10^{-4} cm/s. The reason for this, which is discussed later, is due to reduction of neptunium(V) to neptunium(IV) by the interbed. The kinetics of this reduction process is evidently much slower than that for the sorption process which governs strontium and uranium behavior.

Background Radiation

For the column tests, there are two sources of background radiation. One is the extrinsic radiation that is inherent in any radiological measurement and is independent of the experiment. The extrinsic background was determined by counting samples of the simulants used in the studies. The extrinsic background for the range of alpha energies relevant in this study was 7.5×10^{-4} (CPM/mL)/channel.

The other type of background, referred to here as intrinsic, is due to natural radioactivity in the sedimentary interbed which is leached from the column during the course of the experiment and is subsequently detected when the fractions are analyzed. Intrinsic background was determined by following the normal column test procedure but with the spike excluded. Presented in Figure 4.5 are data for the PWS (2 experiments) and the MPWS (1 experiment). The ordinate is net count rate (after subtraction of extrinsic background) normalized by the number of channels in the region of interest. Each data point is the mean of five measurements of each effluent fraction. Intrinsic background was elevated for the first three DPV, after which it did not differ significantly from zero. In addition, it was the same for both the PWS and the MPWS. The mean of intrinsic background for the first three DPV was 1.72×10^{-3} (CPM/mL)/channel.

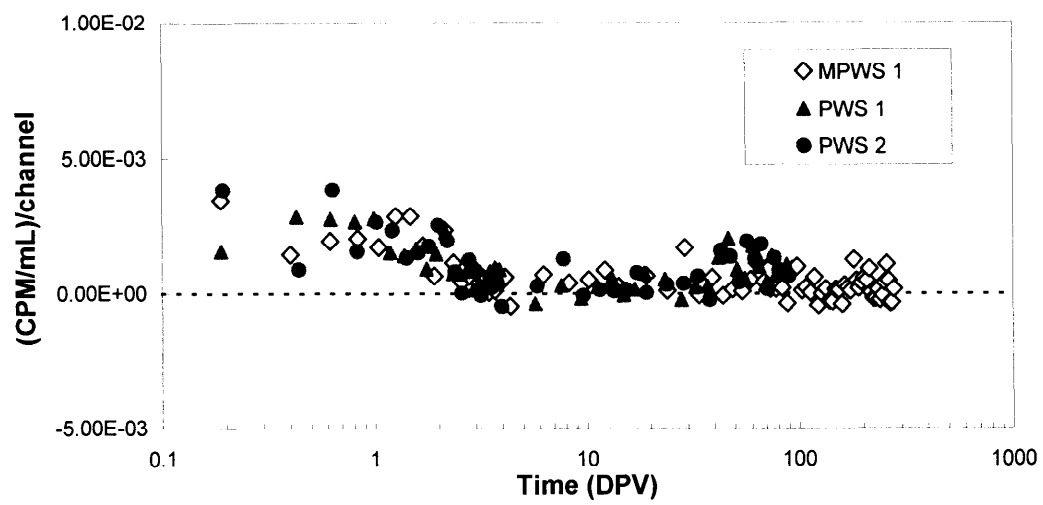


Figure 4.5. Intrinsic background